Quantitative and Qualitative Prediction of Light Absorption by Colored Dissolved Organic Matter in the Coastal Zone

Colin A. Stedmon
Dept. Marine Ecology, National Environmental Research Institute (NERI), University of Aarhus,
Frederiksborgvej 399, DK-4000 Roskilde,
Denmark
phone: +45 4630 1805 fax: +45 4630 1114 email: cst@dmu.dk

Christopher L. Osburn
Dept. of Marine, Earth, and Atmospheric Sciences
North Carolina State University
4150 Jordan Hall
2800 Faucette Drive
Raleigh, NC 27695-8208
Earlier address: Marine Biogeochemistry Section, US Naval Research Laboratory, Washington, DC.
phone: (919) 600-1386 email: closburn@ncsu.edu

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LONG-TERM GOALS

To do describe the distribution and characteristics of colored dissolved organic matter (CDOM) in the coastal zone on the basis of physical water mass mixing. The study site is the Kattegat and Belt Sea at the entrance to Baltic Sea, however the approach is designed for implementation is other regions of Navy interest.

OBJECTIVES

The projects objective is to demonstrate a method for predicting the quantitative and qualitative distributions of CDOM in the littoral zone based on combined model of CDOM biogeochemical cycling and physical oceanography. This approach provides the Navy with an alternative technique by which to gauge the performance of satellite based predictions of CDOM distributions.

APPROACH

The field work of this project was carried out in the Baltic Sea-North Sea mixing zone at the entrance to the Baltic Sea. The Baltic Sea is a large fjord greatly influenced by freshwater inflow from its large drainage basin and having a limited exchange with the North Sea (Atlantic Ocean). As a result its waters have a high content of terrestrially derived organic material. Danish marine monitoring cruises with R/V Gunnar Thorson were used as a sampling platform for the project. The cruises covered 26 stations (Figure 1). Samples were taken for optical and chemical measurements of dissolved organic matter. Data for other water constituents and properties were made available from the monitoring program (temperature, salinity, chlorophyll, nutrient concentrations).

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The focus of the project was on mapping the distribution of CDOM in these waters and linking this to changes in its chemical characteristics and the physical oceanography of the region. In coastal waters and in particular the Baltic Sea – North Sea region CDOM has been shown to behave quasi conservatively and be a useful tracer of water mass mixing (Kalle 1949; Højerslev 1988; Karabashev et al 1993). However despite this Højerslev and Aas (2001) were unable to identify predictable trends in CDOMs characteristics (spectral slope coefficient). With improved methods for estimating S (Stedmon et al 2000) and by expanding an approach for predicting its behavior during mixing (Stedmon and Markager 2003), we strove to reveal resolve this issue.

In order to be able to derive less site specific models in the future which are not so dependent on large calibration data sets, detailed chemical measurements of CDOM were performed. This characterization also served to validate CDOM sources in the region. Dissolved organic carbon (DOC) concentration and stable isotope values (δ^{13}C-DOC) were measured on filtered water samples per Osburn and St-Jean (2007). Further, dissolved lignin was measured on select surface and bottom water samples at stations 444, 905, 925, and 1001, following solid phase extraction onto C_{18} resins (Louchouarn et al. 2001). The spatial distribution meant to capture the flow of terrestrial DOM out from the Baltic Sea through the Danish straits to the mixing zone. The measurement of lignin served as an additional check on the δ^{13}C-DOC values, in which phytoplankton signals may overlap with terrestrial signals.

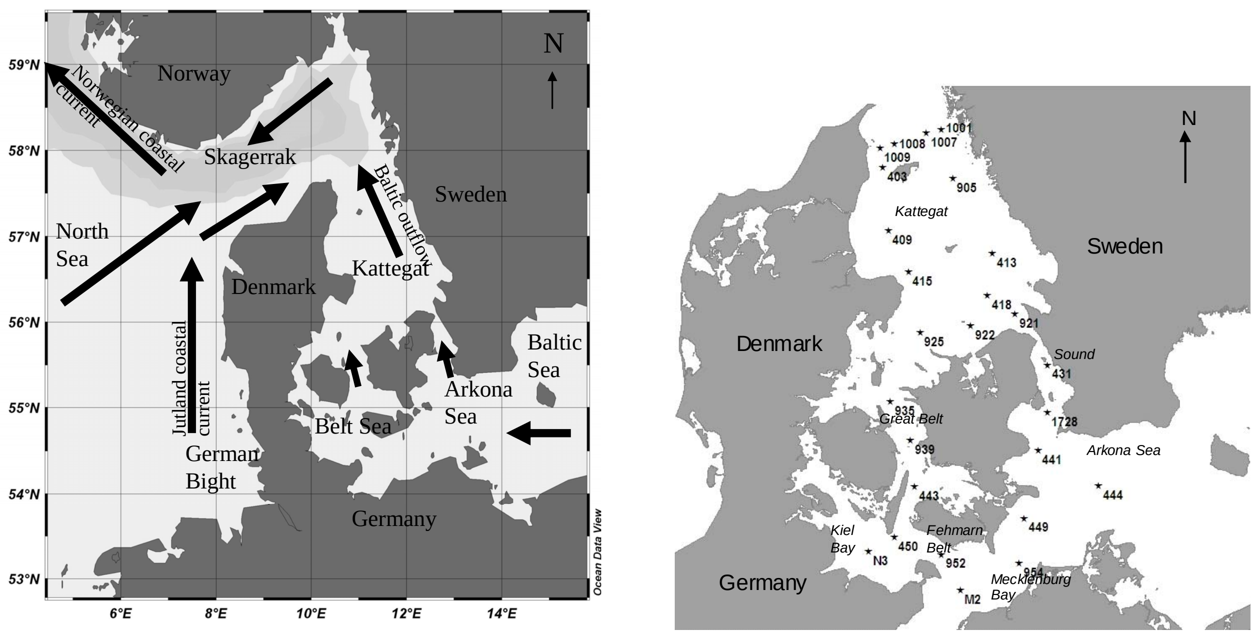

Figure 1. Maps of the study area at the entrance to the Baltic Sea showing the major currents and the monitoring stations sampled. Shown are the eastward Baltic Outflow, the Jutland coastal current and the inflow (westward) from the North Sea to the Baltic Sea. A total of 26 stations were sampled as part of the program.

WORK COMPLETED

The project period was from April 2006 to the end of June 2008. Project planning meetings have been held at NERI in June 2006, February 2007 and during the ASLO/AGU OS meeting in March 2008. A total of seven cruises were carried out, covering 17-24 stations each and resulting in a total of 1016 samples. In addition CDOM absorption data (591 samples) from three earlier cruses was included to give the best possible foundations for the data analysis. The following parameters were measured; CDOM light absorption and fluorescence, dissolved organic carbon, $\delta^{13}C$ of DOM and lignin content. Due to the intensive nature of the lignin characterization this was only carried out on a sub set of samples. Preliminary results from the project were presented at the ASLO/AGU Ocean Sciences meeting in Orlando, 2008.

RESULTS

There are two clear mixing lines CDOM absorption with salinity in these waters (Figure 2a). One representing the mixing of the German Bight water with high a_{300} (>5 m^{-1}) and a salinity of approximately 29, with the North Sea water with low a_{300} (~0.05 m^{-1}) and high salinity (>35). The other line represented the mixing of the Baltic Sea water (salinity < 8, a_{300} ~5 m^{-1}) with an intermediate on the German Bight-North Sea mixing line having a salinity of approximately 32-33 and an a_{300} ~2 m^{-1}. These results suggest that the saline marine end member for the waters of the Baltic Sea consists of a mixture of German Bight water and North Sea water. Data for the spectral slope is shown in Figure 2b. *S* values generally tended to decrease with increasing salinity in an approximately linear fashion from 20 μm^{-1} at salinities below 8, to 18 μm^{-1} at salinities above 32. At high salinities there was a greater variability in *S* values.

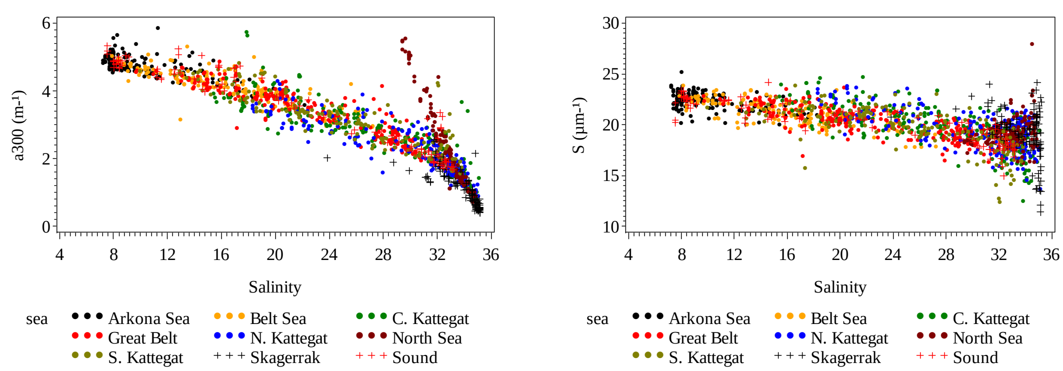

Figure 2. a) Graph of a_{300} for CDOM against salinity revealing two dominant mixing lines apparent. One representing the mixing of the Jutland coastal current water with the central North Sea water and the second representing the mixing of the water flowing out of the Baltic with an intermediate from the previous mixing line. b) Graph of how CDOMs spectral slope (S) varied with salinity. S decreases slightly with increasing salinity in an approximately linear fashion.

From Figure 2 the characteristics of the three end members were determined by averaging the samples at each extreme. With these values and applying a similar approach to that of Højerslev et al (1996) the relative amount CDOM from each of the three end members was determined for each sample. This calculation allows us to split the CDOM spectra into the underlying contribution from each CDOM end member (Figure 3a) for each sample (Figure 3b).

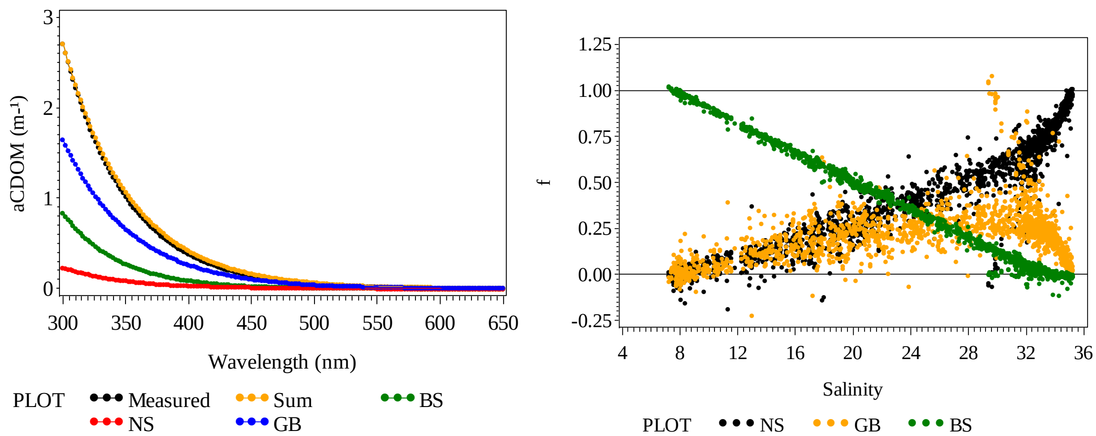

Figure 3. a) An example of a measured and modelled CDOM absorption spectrum, where the model represents the sum of the absorption spectra from CDOM contributions of the three different end members. b) The fraction of each CDOM end member in each sample plotted against salinity. The Baltic Sea fraction decreases approximately linearly with increasing salinity, whilst the remaining fraction is approximately equal between North Sea water and Jutland Coastal Current water.

Under ideal conditions with, for example, fixed precise values of end member characteristics, no analytical error, no instrumental noise, nor autochthonous processes, the values for *f* would only vary between 0 and 1. For the majority of the samples in this dataset this is in fact the case which is encouraging. Values of *f* greater than 1 and below 0 are largely constrained to samples at the extremes representing 100% of each of the three end members and this is purely an artefact of the fact that mean values were used.

From these results it is clear that at salinities below 20, over 50% of the CDOM originates from the Baltic Sea, and the remaining CDOM is relatively evenly split between German Bight and North Sea water. At salinities above 32, there is little influence of Baltic Sea CDOM and the CDOM pool comprises of North Sea and German Bight material. It is clear that the CDOM from the German Bight in the Southern North Sea can be traced into the Belt Sea bottom waters. The inner Danish waters (Southern Kattegat, Great Belt, Belt Sea, Arkona Sea and the Sound) with salinities between 14 and 30 contained on average 23 % German Bight CDOM.

Using these results and the end member characteristics of the three CDOM pools, estimates for *S* values can also be calculated according to the approach in Stedmon and Markager (2003). The differences between the measured and modelled values for a_{300} and S shown in Figure 4.

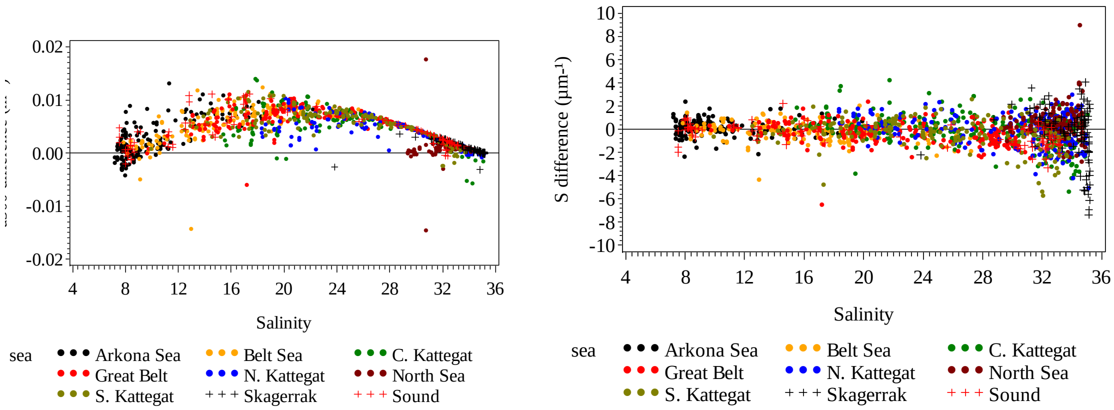

Figure 4. a) Difference between the measured and modelled a_{300} plotted against salinity. Trend shows that there is an additional low intensity source of CDOM at intermediate salinities thought to be local freshwater inputs. b) Difference between the measured and modelled S values plotted against salinity. The plot shows no systematic deviations from zero.

In general the fit to the a_{300} values was very good especially at the two salinity extremes. There was however a systematic increase in the unexplained a_{300} towards a maximum between salinities of 15 and 20 where model estimates were approximately 0.01 m^{-1} lower than measured values (Figure 4a). This deviation decreased approximately linearly as salinities increased further from 24. This represents local fresh water inputs of CDOM into the waters of the Kattegat and Belt Sea that are small but apparently detectable with this approach. They represent 0.25% of the CDOM values at these salinities and are within the detection limits of the spectrophotometric method (Stedmon and Markager 2001). However the systematic pattern with salinity, with peak values at intermediate salinities and a clear linear decrease with increasing further mixing strongly suggests that this trend is due to the conservative mixing of local inputs of CDOM into the Baltic out flow water.

In contrast no overall systematic trends were apparent in the differences in *S* values. However, there remains a greater amount of scatter about zero in the differences between the measured and modelled *S* values, and the scatter increases slightly at higher salinities (Figure 4b) corresponding to samples with low CDOM concentrations (data not shown). One systematic deviation from the model was apparent for samples from the Skagerrak waters with a salinity above 34.5.

In contrast to the results for a_{300}, the impact of local CDOM inputs at intermediate salinities on *S* values was not apparent. Local inputs are of very low intensity in comparison to the three major CDOM pools and therefore have little impact on *S* values (Stedmon and Markager, 2003). CDOM exported from fjords in the region also has very similar *S* values to the range of values found in the Kattegat (Stedmon et al 2000). The close match of the conservative mixing estimates to the measured *S* values indicate on the whole that CDOMs spectral properties in these waters can be modelled relatively easily and that allochthonous supply dominates the distribution on the relevant time scales for mixing in these waters (1-6 months). The combination of continual re-supply and high back ground concentrations of CDOM are a likely reason for this and this is currently being studied further using a 3D hydrodynamic model for water exchange in the region.

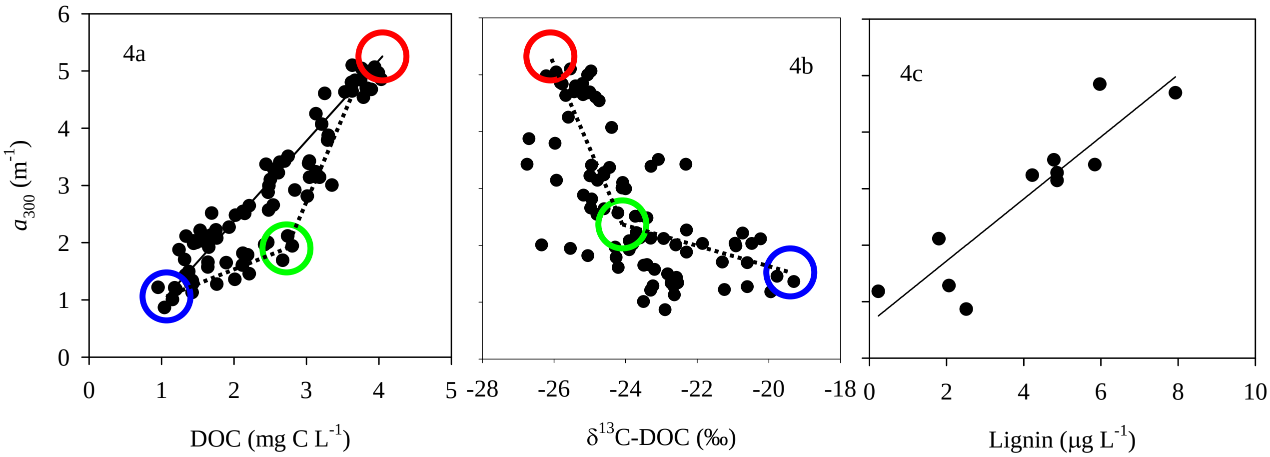

Figure 5. Relationship of CDOM absorption to a) DOC concentration, b) $\delta^{13}C$ and c) lignin concentration. The data support the presence of three major pools of CDOM in these waters, proposed from the absorption data.

The results of the chemical characterisation of CDOM support the trends seen in the optical properties, clearly revealling three major CDOM sources in these waters (Figure. 5a, b). These results are discussed in more detail in the report from N0001408WX21032 (OBosbur). The Batlic Sea CDOM was characterised as having high DOC and lignin concentrations and a δ^{13}C of -26‰. The north sea waters had low DOC and was less depleted (~1 mg C L^{-1}; -20‰). The water originating from the German Bight, was intermediate with a δ^{13}C of 24‰. A regression model for the relationship between DOC concentration and a_{300} returns a value of 0.6 mg C L^{-1} as the nonchromophoric fraction (where absorption is zero, data not shown). This result suggests that CDOM represents about 40% of the DOC for the North Sea water and ~85% of the DOC for the Baltic Sea water.

Most of the qualitative and quantitative variability in CDOMs absorption properties in these waters was modelled by conservative mixing. These findings are advantageous for phytoplankton remote sensing applications in the region where the signal from CDOM has to be taken into account (Karabashev 1992). Additionally the knowledge gained here can be easily assimilated into ecosystem models in order to improve the estimation of photic depth and herein primary productivity. These results emphasise the great potential of carefully validated CDOM measurements in tracing water mass mixing which to date has not been fully exploited by physical oceanographers.

IMPACT/APPLICATIONS

The success of future developments and applications of airborne, satellite and sub-marine optical sensors in these waters is largely dependent on removing the CDOM signal. Dynamical physical mixing models are already used in a wide range of oceanographic research and monitoring applications, however the use of these for predicting CDOM distributions is not widespread. The proposed modeling approach offers a forecasting and nowcasting technique to support the Navy's Littoral Remote Sensing program with estimates of inherent optical properties (IOPs) of water, or water clarity.

RELATED PROJECTS

This work is done in collaboration with Dr. Christopher L. Osburn who is funded under N0001408WX21032. There was a high degree of synergy between this project and another project held by C. Stedmon funded by the Danish Technical Science Research Council. The project is focused on improving fluorescence characterization methods for CDOM and providing increased insight on the correlations between its chemical and optical properties. Project started in 2005 and ended in 2007, with a budget of 1.4 million DKK (approx. US$230,000).

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Stedmon, C.A., Osburn, C.L., and Kragh, T. (in review). Predicting spectral light absorption by CDOM in the Baltic-North Sea mixing zone via water mass mixing. Limnology and Oceanography.

Osburn, C. L.; Stedmon, C. A.: Resolving optical and chemical measurements of terrestrial DOM flux in the North Sea-Baltic Sea mixing zone. ASLO/AGU Ocean Sciences Meeting 2008, Orlando, Florida, USA. (Poster presentation).

Stedmon, C. A.; Osburn, C. L.: Spectral light absorption by CDOM in the North Sea-Baltic Sea mixing zone: Modeling seasonality and dependency on water mass mixing. ASLO/AGU Ocean Sciences Meeting 2008, Orlando, Florida, USA. (Oral presentation).